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CALCULATION OF PHASE EQUILIBRIUM FOR LIQUID PHASE EPITAXY OF InAsSbP QUATERNARY ALLOYS ON InAs SUBSTRATE

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1. Introduction

Photovoltaic devices developed for thermophotovoltaic (TPV) applications have bandgaps from 0.5 eV to 0.75 eV. Most works on TPV devices have concentrated on III−V semiconductors InGaAs on InP (typically E_g = 0.5–0.73 eV, but limited by the lattice mismatch to the high bandgap ranges), or InGaAsSb on GaSb (limited to E_g > 0.5 eV by the miscibility gap). Although III–V ternary and quaternary semiconductors have widely tunable spectral responses the constraints limit the practical range of bandgaps in most of these systems. System modelling results have indicated the advantages of still lower bandgap (< 0.5 eV) TPV cells [1]. A maximum efficiency can be achieved with bandgaps between *0.2–0.5 eV* for black-body sources temperature in the range from 1200K to 2500K. This bandgap range is considerably lower than almost all conventional TPV cells. Thus, there is a need for significant development in both new materials used for TPVs and in processing, to produce high−performance TPV converters with low bandgaps. An alternative to mentioned above TPV structures are less developed epitaxial InAsSbP lattice-matched structures on *InAs* substrates [2, 3]. The InAs/InAsSbP TPV cells have variable bandgaps ranging from 0.3 to 0.5 eV that displace the spectral response to the long-wavelength range, which is impossible to cover by GaSB−based materials.

For successful liquid phase epitaxy (LPE) growth, precise information is required relating to liquidus isotherms lines for the chosen solid composition.

The purpose of the present study is to calculate phase equilibrium for LPE growth of $InAs_{1-x-y}Sb_xP_y$ alloys, as well as to calculate the composition and thickness of grown layers.

2. Calculations of phase equlibria of InAsSbP quaternary alloys

Liquid−solid phase equilibrium calculations were carried out using a simple solution model for the liquid and a strictly regular solution model for the solid. The calculations assume that

$InAs_{1-x-y}Sb_xP_y$ solid can be treated as a ternary mixture of the binary alloys InAs, InSb, and InP (a pseudoternary system), and that

$$In^l + As^l + Sb^l + P^l \Leftrightarrow InAs^s + InSb^s + InP^s .$$

Following the usual approach for binary and ternary III−V materials we write equilibrium expressions involving the chemical potential μ for liquid (*l*) and solid (*s*) components,

$$\mu_A^l + \mu_B^l - \mu_{AB}^s = 0, \quad \mu_A^l + \mu_C^l - \mu_{AC}^l = 0, \quad \mu_A^l + \mu_D^l - \mu_{AD}^l = 0 , \tag{1}$$

where *A, B, C*, and *D* represent In, As, Sb, and P, respectively. The chemical potentials of the solid components are given by

$$\mu_{AB}^s = \mu_{AB}^{s0} + RT \ln \gamma_{AB}^s (1-x-y), \quad \mu_{AC}^s = \mu_{AC}^{s0} + RT \ln \gamma_{AC}^s x, \quad \mu_{AD}^s = \mu_{AD}^{s0} + RT \ln \gamma_{AD}^s y , \tag{2}$$

where μ_{AB}^{s0} is the chemical potential of the pure component *AB*, *R* is the ideal gas constant, *T* is the temperature, and γ^s denotes an activity coefficient. For the quaternary liquid

$$\mu_A^l = \mu_A^{l0} + RT \ln \gamma_A X_A , \tag{3}$$

where μ_A^{l0} is the chemical potential of the component *A*, and X_A is the mole of *A* in the liquid mixture. Replacing *A* in Eq.(3) by *B, C*, and *D* provides expressions for μ_B^l, μ_C^l, and μ_D^l. At temperatures below the fusion temperature of compound *AB* ($T < T_{AB}^F$), the chemical potential of pure *AB* may be related to the chemical potentials of the constituent elements *A, B* by a relationship derived by Vieland on the basis of a thermodynamical cycle

$$\mu_{AB}^{s0}(T) = \mu_A^{sl}(T) + \mu_B^{sl}(T) + \Delta S_{AB}^F (T - T_{AB}^F) + \Delta C_p (T_{AB}^F - T - T \ln \frac{T_{AB}^F}{T}) . \tag{4}$$

Here $\mu_A^{sl}(T)$ is the chemical potential of *A* in the stoichiometric liquid *A*−*B*, ΔS_{AB}^F is the entropy of fusion for compound *AB* and ΔC_p^{AB} is the heat capacity difference between liquid and solid. Similar expressions also exist for the other solid components μ_{AC}^{s0} and μ_{AD}^{s0}.

Neglecting the relatively small contributions from the ΔC_p terms in Eq. (4) and making a substitution of Eqs. (2), (3), and (4) into Eq. (1) give the following expressions:

$$\begin{aligned} RT \ln 4X_A X_B + RT \ln \gamma_A^l + RT \ln \gamma_B^l - RT \ln \gamma_A^{sl} \gamma_B^{sl} - RT \ln \gamma_{AB}^s - \Delta S_{AB}^F (T_{AB}^F - T) - RT \ln(1-x-y) = 0, \\ RT \ln 4X_A X_C + RT \ln \gamma_A^l + RT \ln \gamma_C^l - RT \ln \gamma_A^{sl} \gamma_C^{sl} - RT \ln \gamma_{AC}^s - \Delta S_{AC}^F (T_{AC}^F - T) - RT \ln x = 0, \\ RT \ln 4X_A X_D + RT \ln \gamma_A^l + RT \ln \gamma_D^l - RT \ln \gamma_A^{sl} \gamma_D^{sl} - RT \ln \gamma_{AD}^s - \Delta S_{AD}^F (T_{AD}^F - T) - RT \ln y = 0, \end{aligned} \tag{5}$$

under the restriction that

$$X_A + X_B + X_C + X_D = 1 . \tag{6}$$

For a quaternary liquid the activity coefficient γ_A^l is given by

$$RT\ln\gamma_A^l = \alpha_{AB}^l X_B^2 + \alpha_{AC}^l X_C^2 + \alpha_{AD}^l X_D^2 + X_C X_B(\alpha_{AC}^l + \alpha_{AB}^l - \alpha_{BC}^l) + \\ + X_D X_B(\alpha_{AD}^l + \alpha_{AB}^l - \alpha_{BD}^l) + X_C X_D(\alpha_{AD}^l + \alpha_{AC}^l - \alpha_{CD}^l), \quad (7)$$

with similar expressions for γ_B^l, γ_C^l, and γ_D^l. Here α_{AB}^l is the interaction parameter between components *A* and *B* in the liquid. For the pseudoternary solid solution, we treat the solid as a mixture of three components such that,

$$RT\ln\gamma_{AB}^s = \alpha_{AB-AC}^s x^2 + \alpha_{AB-AD}^s y^2 + xy(\alpha_{AB-AC}^s + \alpha_{AB-AD}^s - \alpha_{AC-AD}^s),$$
$$RT\ln\gamma_{AC}^s = \alpha_{AB-AC}^s (1-x-y)^2 + \alpha_{AC-AD}^s y^2 + (1-x-y)y(\alpha_{AB-AC}^s + \alpha_{AC-AD}^s - \alpha_{AB-AD}^s), \quad (8)$$
$$RT\ln\gamma_{AD}^s = \alpha_{AB-AD}^s (1-x-y)^2 + \alpha_{AC-AD}^s x^2 + (1-x-y)x(\alpha_{AB-AD}^s + \alpha_{AC-AD}^s - \alpha_{AB-AC}^s),$$

where α_{AB-AC}^s is the interaction parameter between components *AB* and *AC* in the solid. In the present work, we have used the data [4] presented in Table 1. Mole fractions of each element in the liquid phase can be determined by solving equations (5) and (6) for given *x, y,* and *T*.The results of numerical simulations under condition when $InAs_{1-x-y}Sb_xP_y$ layers lattice−matched to InAs substrate (y=2.23x) are performed by Newton method and presented in Fig.1.

Table 1

Thermodynamic Parametrs	System	Value
Melting point T_{AB}^F / K	InAs	1215
	InSb	798
	InP	1343
Entropia of fusion ΔS_{Ab}^F (cal mol^{-1})K^{-1}	InAs	14.52
	InSb	14.32
	InP	14.0
Liquid phase interaction parameters α_{AB}^l/(cal mol$^{-1)}$	As−Sb	750
	As−P	1500
	In−As	−6070
	In−Sb	−3980
	In−P	4500−4T
	Sb−P	4500
Solid phase interaction parameters α_{AB-AC}^l /(cal mol$^{-1)}$	InAs−InSb	2250
	InAs−InP	400
	InSb−InP	6000

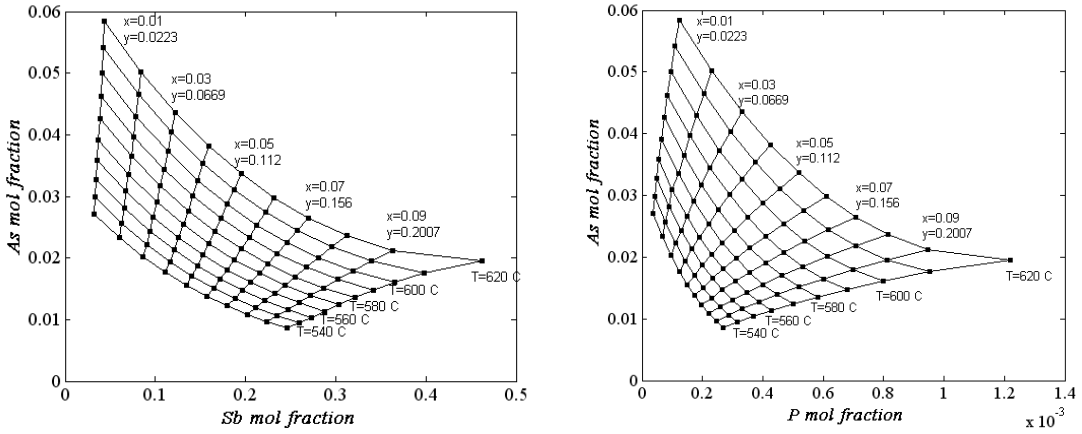

Fig. 1. Solid−liquid phase diagram for $InAs_{1-x-y}Sb_xP_y$ plotted as a function of the atomic mol fractions of P−As and Sb−As in the melt and the concentration of InP (y=2.23x) in the solid equilibrium.

3. Calculations of $InAs_{1-x-y}Sb_xP_y$ layers thickness grown by LPE

We have carried out the calculations of thickness of $InAs_{1-x-y}Sb_xP_y$ layers lattice-matched to InAs substrate for step−cooling LPE, because this technique provides high quality of grown layers. In this technique the epitaxial growth is realized from solution super cooled by $\Delta T = T_1 - T_2$. T_1 is the initial temperature of saturated solution (In+As+Sb+P) which is in an equilibrium with InAs substrate and T_2 is the temperature of supercooled solution. The results of our experiments have shown that the component compositions are uniform along the layer thickness. This result allows us to assume that at the end of growth process the solution is in the equilibrium with grown layer at the temperature T_2.

The thickness of LPE layer is

$$h = \frac{\Delta m_{InAs} + \Delta m_{InSb} + \Delta m_{InP}}{S \cdot d_{InAsSbP}(x,y)}, \tag{9}$$

where S is the area of epilayer, $d_{InAsSbP}(x,y)$ is the density of $InAs_{1-x-y}Sb_xP_y$ quaternary alloy,

$$\Delta m_{InAs} = m_{InAs} - m_{InAs}', \quad \Delta m_{InSb} = m_{InSb} - m_{InSb}', \quad \Delta m_{InP} = m_{InP} - m_{InP}'.$$

Here $m_{InAs}, m_{InSb}, m_{InP}$ and $m_{InAs}', m_{InSb}', m_{InP}'$ are the masses of binary components dissolved in the solution In+As+Sb+P at the temperature T_1 and T_2. Expressing these masses in terms of atomic fractions of components X_i and X_i' at T_1 and T_2 for the epilayer thickness, we can write

$$h = \frac{1}{S \cdot d_{InAsSbP}(x,y)} \cdot \frac{m_{In}}{\mu_{In}} \cdot \left[\mu_{InAs} \left(\frac{X_{As}}{1-2X_{As}-2X_{P}-2X_{Sb}} - \frac{X'_{As}}{1-2X'_{As}-2X'_{P}-2X'_{Sb}} \right) + \right.$$
$$+ \mu_{InP} \left(\frac{X_{P}}{1-2X_{As}-2X_{P}-2X_{Sb}} - \frac{X'_{P}}{1-2X'_{As}-2X'_{P}-2X'_{Sb}} \right) + \qquad (10)$$
$$\left. + \mu_{InSb} \left(\frac{X_{Sb}}{1-2X_{As}-2X_{P}-2X_{Sb}} - \frac{X'_{Sb}}{1-2X'_{As}-2X'_{P}-2X'_{Sb}} \right) \right].$$

The density of $InAs_{1-x-y}Sb_xP_y$ expressed by the densities of binary components ($d_{InAs}, d_{InSb}, d_{InP}$) and lattice constants of binary components and quaternary alloy ($a_{InAs}, a_{InSb}, a_{InP}, a_{InAsSbP}$) has the form

$$d_{InAsSbP} = \frac{\left[(1-x-y) d_{InAs} a^3_{InAs} + y d_{InP} a^3_{InP} + x d_{InSb} a^3_{InSb} \right]}{a^3_{InAsSbP}(x,y)}. \qquad (11)$$

The results of our calculations we have used for the growth of $InAs_{1-x-y}Sb_xP_y$ layers of two different compositions *y=14%* and *y=8%* lattice-matched to InAs substrate (*y=2.23x*). The growth temperature was 550°C and $\Delta T = 5\,^{o}$C. The SEM−EDX investigations have shown that the compositions of $InAs_{1-x-y}Sb_xP_y$ layers are in good agreement with theoretical modeling results.

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REFERENCES

1. G.D. Cody. "4th NREL Conference" in TPV Generation of Electricity, AIP Conference Proceedings, v. 460, 58 (1998).
2. V.A. Gevorkyan et al. Thin Solid Films, v.451/452, 124 (2004).
3. M.G. Mauk and V.M. Andreev. Semicond. Sci. Technol., v.18, S191 (2003).
4. H.Mani et al. J. Cryst. Growth, v. 121, 463 (1992).